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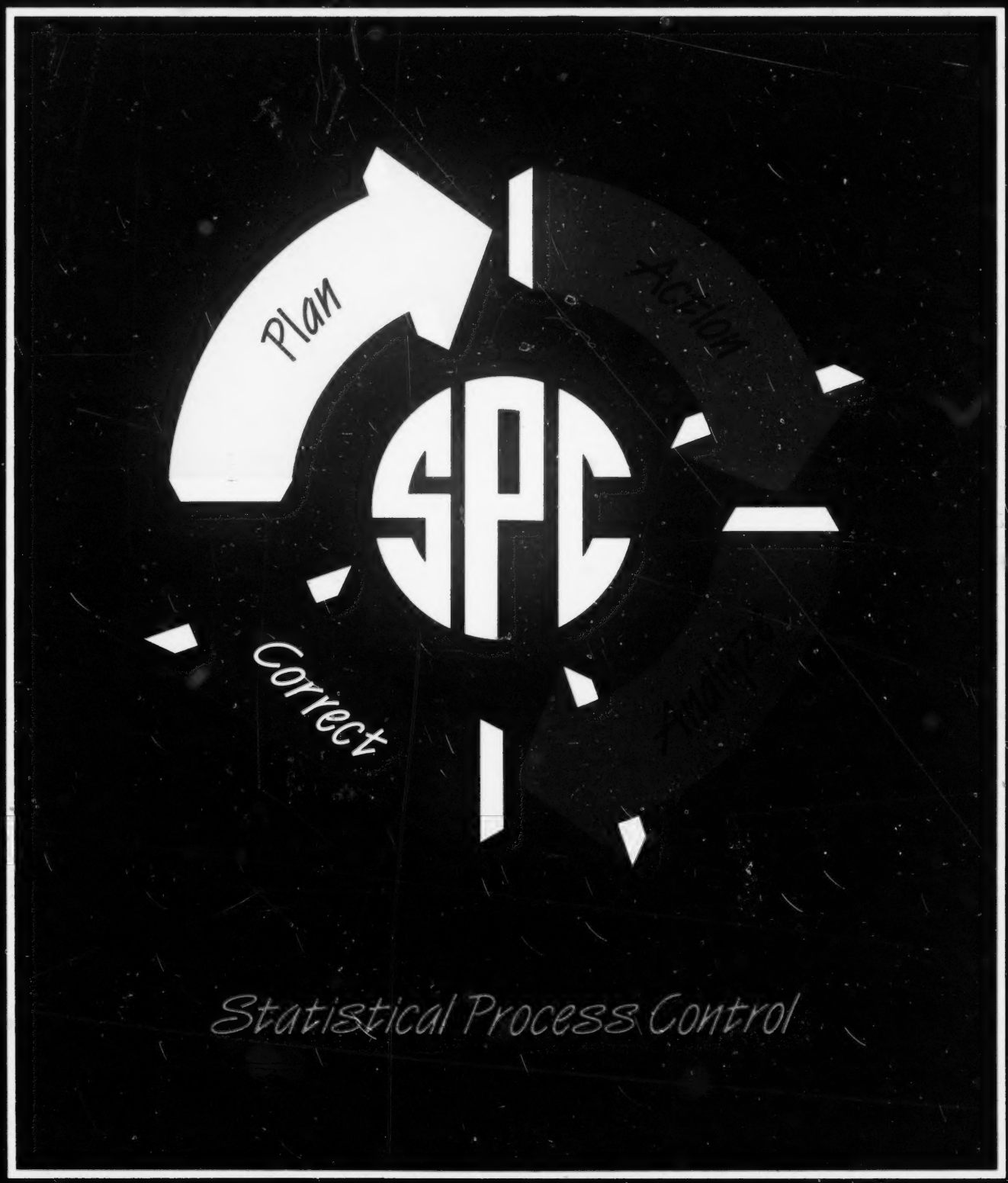

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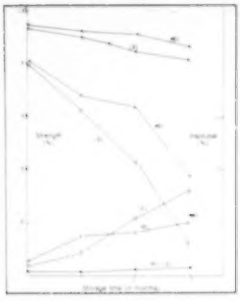

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Cover artwork by Akron artist Judy Everett

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Business Briefs

Acquisitions, expansions

Exxon Chemical Americas has begun production of bromobutyl at its Baton Rouge, LA chemical plant. The company's French affiliate is expanding capacity for ethylene-propylene rubbers at Notre Dame de Gravenchon by 30% to 65,000 tons per year.

Goodyear has agreed to buy up to 63% of the common stock of **Brad Ragan, Inc.** a retailer of new tires and manufacturer of retreaded tires and a leading retreader of off-road tires. Goodyear will operate Brad Ragan Inc. as a separate subsidiary. Goodyear formed **Retread Systems Inc.**, a wholly owned subsidiary comprised of Long Mile Rubber and AMF Tire Equipment, two companies recently purchased by Goodyear. Goodyear also opened a million dollar research and quality control laboratory in Singapore. The lab will aim at improving natural rubber quality.

Firestone plans to spend $240 million in capital expenditures in 1986. $100 million will be for projects in the company's raw material and tire operations in North America; About $67 million for expansion of tire facilities in Brazil, Argentina and Venezuela, and production rationalization in Europe; $43 million for the retail outlet operation; and $20 million for the Diversified Products area.

Chardon Rubber acquired **Beebe Rubber** and **Webster Rubber**, formerly divisions of Mohawk Rubber. Beebe Rubber, Nashua, NH, will be operated as a subsidiary of Chardon, while Webster Rubber, Sabbatus, ME., will become a division of Beebe.

Carlisle Corp.'s SynTec Systems is investing $10 million in new equipment which will allow the company to produce an additional 265 million square feet of single-ply membrane for roofing.

Lydall, Inc. has completed the purchase of **Pantasote's** Elastomer Products Division in Clifton Forge, VA a molded rubber products manufacturer.

Witco's Organics Division established a new laboratory devoted exclusively to surfactant technology for emulsion polymerization at one of its technical centers in Chicago.

Degussa Corp. started operations at a new applications research and technical service laboratory in Allendale, NJ. Completion of the 21,000 sq. ft. facility is expected at years end.

Fruehauf Corp. sold its Pro-Par truck tire retreading operations to **Pro Tread Corp.**, Famington Hills, MI. Sale included retreading facilities in Fort Worthy, TX; Howell, MI; York, PA; East Hartford, CT, and Charlotte, NC.

Ausimont Compo N.V. acquired **Allied-Signal's** fluoropolymer business units for $55 million. Plant facilities in Orange, TX and Elizabeth, NJ were included in the sale.

Lonza Inc. has completed its acquisition of **Glyco, Inc.**, Norwalk, CT. Glyco will initially be a fully operating subsidiary.

Glenro Inc. has opened a new web processing laboratory at its Patterson, NJ facility.

MG Industries has under construction a multi-million dollar air separation unit in Spartanburg, SC that will be operational in early 1986.

Smith & Nephew, Columbia, SC has merged its OpSite and wound care divisions with the Perry division of Affiliated Hospital Products, acquired by Smith & Nephew in 1985. The new division will operate from the Perry division's facilities in Massillon, OH.

RMA rubber report through November 1985 (figures in metric tons)

	Cumulative 1985	Cumulative 1984	% Change 85 vs 84
New Rubber			
New rubber available	2,754,530	2,963,302	-7 05
Imports	979,227	958,528	2 16
Exports	332,203	354,806	-6 37
Apparent Consumption	2,418,559	2,598,297	-6 15
Natural Rubber			
Imports	723,510	735,436	-1 62
Exports	35,860	30,370	18 08
Apparent Consumption	698,834	696,583	32
% Total new rubber	28 65	26 80	
Synthetic Rubber			
Production	1,775,303	2,004,774	-11 45
Imports	255,717	223,090	14 63
Exports	296,343	324,436	-8 66
Apparent Consumption	1,739,725	1,901,714	-8 52
% Total new rubber	71 34	73 19	
SBR			
Production	750,372	889,287	-15 62
Imports	89,110	66,593	33 81
Exports	76,625	96,628	-20 70
Apparent Consumption	777,173	850,214	-8 59
Nitrile			
Production	51,964	61,652	-15 71
Imports	10,919	10,989	- 64
Exports	6,097	7,662	-20 43
Apparent Consumption	56,527	60,761	-6 97
Polybutadiene			
Production	306,846	330,545	-7 17
Imports	66,411	61,617	7 78
Exports	22,016	22,702	-3 02
Apparent Consumption	347,241	380,565	-8 76
Ethylene-Propylene			
Production	204,051	200,840	1 60
Imports	1,073	1,193	-10 06
Exports	33,933	31,358	8 21
Apparent Consumption	165,157	162,741	1 48
Butyl, Polychloroprene, Polyisoprene, Silicone and other Synthetic Elastomers			
Production	462,069	522,450	-11 56
Imports	88,204	82,698	6 66
Exports	157,672	166,086	-5 07
Apparent Consumption	393,625	447,432	-12 03

Contracts, licenses

Uniroyal Chemical appointed **Harwick Chemical** as exclusive distributor of its millable urethanes throughout the U.S.

Montedison USA appointed **Akron Chemical** as exclusive distributor of its line of organic peroxide vulcanizing/crosslinking agents to the rubber industry east of the Rocky Mountains.

Exxon Research and the Commerce Department's **National Bureau of Standards** have entered into an agreement for the development a new small angle neutron scattering instrument, a nondestructive technique with applications in the polymer industry.

Business Briefs

BP Chemicals has licensed **Reichhold Chemicals** to manufacture BP's phenolic foam resin in North America.

Pacific Smelting has signed agreements with **AM&S Europe Ltd.** Bristol, UK and **Sulphide Corp.**, Melbourne, Australia to sell those companies zinc products in the U.S.

Seitetsu, Osaka, Japan has licensed its superabsorbent polymer technology to **Norsolor**, a subsidiary of CdF Chimie, Paris, France.

Financial statements

Armstrong Rubber reported first quarter net sales of $202.1 million and net income of $1.5 million.

Cabot Corp. reported a net income loss of $86.3 million for 1985 with net sales reaching $1.4 billion.

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Eagle-Picher announced a net income loss of $119.8 million for 1985 on net sales of $641.7 million.

Exxon reported net income of $4.8 billion in 1985 on revenues of $93.2 billion.

GenCorp reported 1985 net income of $75.2 million on sales of $3 billion.

Goodyear's net income for 1985 was $412.4 million on sales of $9.6 billion.

Lydall, Inc. reported earnings for 1985 of $4.2 million on sales of $105 million.

NL Industries reported 1985 net income of $21.5 million on sales of $377.1 million.

Rubbermaid had net earnings in 1985 of $57.1 million on sales of $671 million.

Sheller-Globe reported net income for 1985 at 36.7 million on sales of $917.7 million.

Standard Products' net earnings for the second quarter were $5.5 million on sales of $106.4 million.

Markets, news

Shipments of passenger tires in the U.S. were off slightly in 1985 according to the Rubber Manufacturers Association year end figures. Total shipments dropped less than 1% to 200.9 million units. Original equipment shipments increased 7.5% to 54.8 million units but the replacement market was off 2.1% at 141.4 million. Shipments of truck and bus tires increased just less than 1% to 41.1 million units. There was a 7.4% increase in the number of imported radial passenger tires with the total reaching 29.7 million units.

Worldwide consumption of synthetic rubber increased 3% in 1985 and should increase 15% by 1990 according to the International Institute of Synthetic Rubber Producers. Total new rubber consumption is expected to rise

RMA tire shipments & production report through December 1985 (figures in thousands of units)

Passenger Tires	YTD 1985	YTD 1984	% Change
Shipments			
Original Equipment	54,838	50,993	+7.54
Radial	45,773	42,728	+7.13
Replacement	141,455	144,580	−2.16
Radial	115,412	109,498	+5.40
Export	4,625	6,064	−23.73
Radial	3,555	4,375	−8.74
Total	200,918	201,637	−0.36
Radial	164,740	156,601	+5.20
Production	162,583	172,934	−5.99
Radial	130,952	131,512	−0.43
Ending Inventory	—	—	—
Radial	—	—	—
Truck & Bus Tires			
Shipments			
Original Equipment	7,698	7,777	−1.02
Radial	4,895	4,108	+19.16
Replacement	32,098	31,707	+1.23
Radial	14,099	11,332	+24.42
Export	1,335	1,333	+0.15
Radial	723	593	+21.92
Total	41,131	40,817	+0.77
Radial	19,717	16,033	+22.98
Production	33,389	36,441	−8.38
Radial	14,865	13,753	+8.09
Ending Inventory	—	—	—
Radial	—	—	—

from 12.8 metric tons in 1985 to 14.7 mmt by 1990. The sharpest gains will take place in Asia and Latin America, while North America and Europe will post modest growth in the next five years the IISRP predicts.

Asia will represent the largest volume growth with a 19% increase by 1990. Latin America is expected to grow by over 5% each year for an overall growth of 27% by 1990. Meanwhile, consumption in Europe will go up by 10%. North America will post an increase of 5% by the end of this decade. In the same period, the Centrally Planned Economy Countries (CPEC), including Russia and Eastern Europe, will show a growth rate of about 3.6% a year. The People's Republic of China's consumption is forecast to increase almost 10% a year throughout the rest of this decade. Synthetic rubber is projected to represent consistently about two-thirds of total rubber demand, and tire products will continue to consume about 55% of all synthetic rubber.

Total new rubber consumption forecast worldwide (excluding centrally planned economy countries) (thousand metric tons)

	1984	1985	1986	1990
SBR solid	2467	2404	2441	2652
SBR latex*	301	317	325	351
Polybutadiene	969	993	1008	1102
Ethylene-propylene	408	430	444	513
Polychloroprene	250	254	256	270
Nitrile — solid and latex	193	196	199	219
Other synthetic**	813	757	770	870
Total synthetic	5401	5351	5443	5977
Natural rubber	3316	3514	3610	3972
Total new rubber	8717	8865	9053	9949
Synthetic percent (%)	62.0	60.4	60.1	60.1
Carboxylated SBR latex	743	799	804	887

*Excluding carboxylated latex

**Includes butyl and polyisoprene rubbers

New rubber consumption forecast worldwide forecast by region (thousand metric tons)

Synthetic Rubber	1984	1985	1986	1990
North America	2,209	2,033	2,041	2,135
W. Europe, Africa, M. East	1,570	1,585	1,615	1,739
Asia and Oceanica	1,144	1,245	1,266	1,481
Latin America	478	489	521	622
Total	5,401	5,351	5,443	5,977
Natural Rubber				
North America	839	903	902	936
W. Europe, Africa, M. East	983	1,012	1,031	1,096
Asia and Oceanica	1,296	1,398	1,465	1,705
Latin America	198	201	212	235
Total	3,316	3,514	3,610	3,972
Total Rubber				
North America	3,048	2,936	2,943	3,071
W. Europe, Africa, M. East	2,553	2,596	2,646	2,835
Asia and Oceanica	2,440	2,643	2,731	3,186
Latin America	676	690	733	857
World (excluding CPEC)	8,717	8,865	9,053	9,949

Eastern Europe	1984	1985	1986	1990
Synthetic rubber	2,600	2,820	2,955	3,350
Natural rubber	435	430	440	400
Total new rubber	3,035	3,250	3,395	3,750
% synthetic	85.7	86.8	87.0	89.3
China/Asian CPEC				
Synthetic rubber	184	265	290	395
Natural rubber	332	425	460	626
Total new rubber	516	690	750	1,021
% synthetic	35.7	38.4	38.7	38.7
Total CPEC				
Synthetic rubber	2,784	3,085	3,245	3,745
Natural rubber	767	855	900	1,026
Total new rubber	3,551	3,940	4,145	4,772
% synthetic	78.4	78.3	78.3	78.5
Total world				
Synthetic rubber	8,185	8,436	8,688	9,722
Natural rubber	4,082	4,369	4,510	4,998
Total new rubber	12,268	12,805	13,198	14,720
% synthetic	66.7	65.9	65.8	66.0

Rubber consumption in tire and tire products by polymer type; by region (excludes CPEC)

	% Tire and tire products, 1985					
	Western Europe	North America	Asia & Oceanica	Latin America	Africa & M. East	Weighted Average
SBR solid	67.0	71.9	70.1	70.0	60.0	69.6
SBR latex	6.0	6.2	3.1	30.0	2.0	6.1
Polybutadiene	72.0	76.5	68.6	88.0	90.0	74.8
Ethylene-propylene	0.0	6.0	10.6	2.0	0.0	7.4
Chloroprene	0.0	0.0	0.0	0.0	0.0	0.0
Nitrile	0.0	0.0	0.0	0.0	0.0	0.0
Other synthetic*	64.0	50.1	75.0	83.0	80.0	62.6
Total synthetic	49.0	53.9	56.9	69.0	61.0	54.4
Natural	65.0	73.6	63.4	81.0	78.0	67.7
Total rubber	55.0	60.0	59.0	72.0	70.0	59.2

*Includes butyl and polyisoprene

Automotive elastomers: applications, challenges

by T.J. Mao, General Motors Research Laboratories

Introduction

Over 20 years ago, Ralph Wolf[1], who was a rubber chemist and one of the most talented and prolific writers on rubber[2], wrote "Civilization is wholly dependent upon rubber. It is a material of myriad uses, totally unlike anything the world had previously known. . . . It is indispensable in transportation, in communication, — in cushioning our bodies and protecting our senses from the jars and jolts, the noise and tumult of modern life."

For these same reasons, rubber is used in very many applications in the automotive industry. However, the volume of rubber used in the car is decreasing due to downsizing and to the availability of competitive materials. In this article, the current uses and the new challenges and potential applications of elastomers in the automotive industry will be discussed.

Uses of elastomers in automobiles

The automotive industry is a major consumer of elastomers. In an average automobile, about 20 kg of polymer are used in making 63 kg of various rubber compositions for non-tire automotive applications. In contrast, 24 kg of polymer were used for making elastomer parts for a 1979 car. Forecasts of the future growth of elastomers are not very encouraging[3,4]. Projection of rubber demand through 1988 shows an annual growth rate of 2.3% which is below the generally accepted GNP projections of 3 to 4% annually. The decrease in demand is, in part, due to the decrease[5] in total rubber consumption for automotive tire and non-tire applications, as seen in table 1 based on the best available estimate.

The current non-tire uses of elastomers in automobiles can be grouped into the following categories:

Elastomer parts for isolation of bumps and vibrations

These include engine mounts, torsional dampers, jounce bumpers, strut mounts, seat foam, and several other parts. The main requirement for the elastomers used in these parts is that they damp out vibrations of different amplitudes and frequencies ranging from engine noise all the way down to road vibrations. Another essential characteristic is that the damping characteristics and the dynamic properties of these elastomers should not vary much with temperature or frequency of vibration. This latter property is needed to ensure consistent car riding characteristics in cold winters as well as hot summers and on different road surfaces.

Table 1 — amount of elastomer used in an average car

Year	Amount polymer (elastomer), kg
1976	57.5
1979	43.0
1985	39.0
1986	38.5
1987	38.0
1988	37.0

Elastomer components for containing and/or carrying fluids

These components include seals, gaskets, and hoses. Each component is formulated and designed to handle one or more of the many fluids used in automobiles such as fluorinated hydrocarbons (Freons), engine oils, gasolines, hydraulic fluids, and silicone fluids. The main function of these parts is to contain the fluids under all environmental conditions. In many of these applications, retention of properties after prolonged heat aging and retention of flexibility at low temperatures are essential.

In recent years, new performance demands have been placed on these parts because of the many changes taking place in the types and properties of automotive fluids. For example, changes in engine oils were introduced in order to prolong the useful life of the oils at high operating temperatures. To accomplish this, new additives were placed in these oils. Some of these additives were found to react with and degrade some of the elastomer components used in contact with the oils[6,7].

In recent years, we have witnessed the incorporation of several additives in gasoline in order to improve the octane number or to simply extend the gasoline. Some of these additives are ethanol, methanol and methyl t-butyl ether. The addition of these ingredients changes the solubility parameters of the gasoline and, hence, the degree of swelling of the different fuel system elastomers in these mixtures[8,9]. In some instances, it is necessary to change the composition or the elastomer type used for fabricating some of the components in the fuel system in order to ensure proper performance.

Another difficulty with the handling of gasoline has been the generation of partially oxidized gasoline (sour gasoline) in cars using fuel recirculation. Peroxides found in sour gasoline attack elastomers to varying degrees and by different mechanisms[10]. The use of elastomers susceptible to peroxide attack was discontinued in cars with fuel recirculation.

Elastomer components for protection against environment and wear

These components include weatherstrips, front drive axle boots and floor mats. The properties needed for these parts include resistance against wear and tear, fatigue resistance, and, for some applications, low compression set and good oil resistance. The wider use of front wheel drive vehicles created many challenges for the development of a new elastomer composition for the axle boot that will endure the high mechanical stresses and high temperature environment encountered in this application.

In another application, the demand for lower door closing effort necessitated the development of low density elastomer sponge. Intensive investigations were conducted in our laboratories[11] to characterize and identify the processing, morphology and property relationships for low density sponge in order to improve the wear and tear resistance and prolong the useful life of

the sponge in weatherstrip applications.

Elastomers for electrical insulation
Many elastomers including ethylene-propylene-diene (EPDM) rubber and silicone rubber are used in electrical cables and in wiring to insulate the conducting core and protect it against the environment. The important properties required in these elastomers are excellent electrical insulation, even at very high voltages, and excellent aging properties at high temperatures since many of the wires and cables are used under the hood in close proximity to the engine.

Elastomers for improving appearance
Elastomers are used for exterior body parts to perform many functions including improving the appearance. Examples of these include sight shields and body side moldings. High modulus, excellent surface appearance, paintability and resistance to aging by the environment are some of the properties required for elastomers used in these applications.

Elastomers for precision parts
The elasticity of elastomers and their ability to seal against hard surfaces are properties which make them suitable for use as precision metering components such as the carburetor pump cup and the carburetor needle valve. In addition to flexibility, dimensional stability under service conditions including contact with automotive fluids is a major requirement for the elastomer compositions used in these applications.

Elastomers for modifying the properties of plastics
In recent years, the major expansion of elastomers has been as additives in plastics to improve impact strength. Currently, there are many commercial elastomer-plastics compositions with widely different properties extending from high temperature plastics containing elastomers for improving the impact strength to thermoplastic elastomers which are conventional elastomers containing compatible semicrystalline plastics to act as crosslinks under ambient conditions. Elastomers are also added into plastics to modify other properties such as paintability and platability. Many of these elastomer-plastics compositions are used in automotive applications.

These are the major uses of elastomers in the automotive industry. Let us now examine the challenges that lie ahead.

Challenges for elastomers in automotive applications
As all of us are aware, the continuing concern for improved fuel economy has resulted in a significant downsizing and redesign of the automobile. As a consequence, the engine compartment became smaller and more difficult to cool, and the underhood temperature increased appreciably. While a decade ago, elastomers were required to endure a 100°C environment, they are now expected to perform well (and last the life of the car) under a 120°C in-service temperature. We expect that, in the near future, they will be required to live in a 150°C environment for over 100,000 miles.

As a result of the increased underhood temperature, changes in other materials, such as greases, oils and hydraulic fluids, had to be made so that these materials would be capable of performing at the new temperatures. Since, in many instances, elastomers are used to contain these materials, the interactions between them and the elastomers had to be reexamined. There have been cases in which the new fluids degrade some of the elastomer components designed to contain them.

Aside from the temperature factor, there also have been significant changes in the nature of automotive fuels. Additives, such as ethanol, methanol and methyl t-butyl ether, are now being placed in gasoline in order to extend it or improve its octane number. As was mentioned earlier, these additives change the solubility characteristics of the fuel and, hence, the compatibility of elastomers with the new fuels.

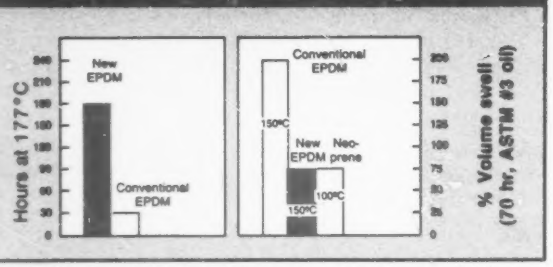
A related concern is the permeability resistance of elastomers to hydrocarbon fluids. Government regulations allow only a certain amount of hydrocarbons to escape to the atmosphere through evaporation. This places a new demand on elastomeric hoses.

Because of these new demands, alternate materials, such as plastics, are being considered for components currently made of elastomers. The rubber industry is being challenged to produce (1) new elastomer materials that will perform well in the new automotive environment and (2) new processes to make elastomers more economically competitive in order to maintain and expand its share of the automotive market. The challenge even extends to the development of new elastomeric components that will improve the durability or the performance of the automobiles. It is well known that many industrial and university laboratories have active research programs on designing new elastomer structures, understanding filler-elastomer interactions and developing thermoplastic elastomers that can be more easily processed than conventional elastomers. There is not enough time to cover all the significant work being carried out in the scientific community. Instead, this article will concentrate on only a few of the new demands being placed on automotive elastomer components and some of the research efforts at GM Research Laborities (GMR) being carried out to meet these challenges.

Examples of new requirements
Elastomers with improved high temperature performance
As it was mentioned earlier, the downsizing of the automobile resulted in higher underhood temperatures and created a need for high temperature fuel resistant as well as non-fuel resistant elastomers. The current high temperature elastomers including silicones, fluorocarbons and hydrogenated nitrile elastomers meet the needs for specific automotive applications, but they cannot be used for most applications because they are too expensive, and also, in some instances, they do not have all the required properties. From our prospective, as a user, there exists a gap between inexpensive general purpose elastomers, such as nitrile and EPDM, and expensive silicones and fluorocarbon elastomers. What we need now are general purpose elastomers that will be able to endure a 150°C projected underhood temperature for the lifetime of the vehicle.

An attempt towards meeting this goal was made at GMR. In one of our investigations aimed at the radiation curing of EPDM, we discovered an antioxidant system that can survive the free radical crosslinking of EPDM

Figure 1 — heat resistance measured as hours at 177°C for 50% retention of original elongation, and oil resistance measured as percent swell for new EPDM versus conventional EPDM



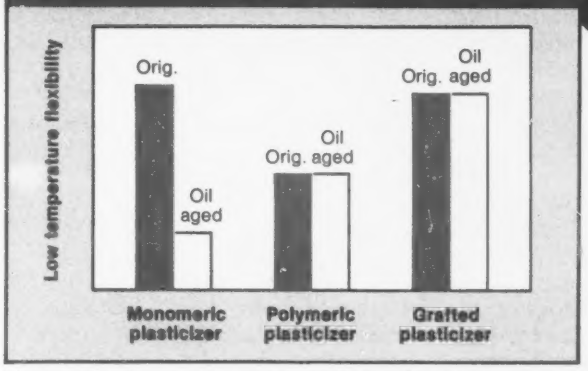
by radiation or by peroxide and produce an elastomer with vastly improved heat aging resistance[12]. The antioxidant system consisted of a hindered phenol, a metal oxide and a chlorinated hydrocarbon. When this system was used in an EPDM formulation containing a peroxide and a coagent as curatives, the heat resistance of the EPDM under the accelerated aging condition of 177°C improved from 30 hours for conventional EPDM to 180 hours (Figure 1). An added advantage was that the oil resistance of this new EPDM formulation also improved as shown in figure 1. The volume swell of the elastomer at 150°C in ASTM #3 oil was reduced from 200% for the conventional EPDM to only 75% for the new composition. This makes the oil resistance of the new formulation comparable to that of neoprene. Similar R&D efforts for further improvement of the heat resistance of EPDM and other elastomers are needed to meet the challenge of increased underhood temperatures.

Low temperature flexibility and oil resistance

In the automotive industry, oil resistant elastomers are essential materials used to fabricate parts such as grease and oil seals, boots, O-rings and hoses. Unfortunately, these elastomers have inherently poor low temperature flexibility, because the molecular structures which give rise to the oil resistance, also result in greater stiffness at low temperatures. Nitrile rubber, a widely used oil resistant elastomer, is a prime example. As the acrylonitrile content is increased, the swell in oil is reduced. This effect is accompanied by an increase in low temperature stiffness. Plasticizers are normally used to improve the low temperature flexibility. However, in the case of elastomers used for parts in contact with hydrocarbon fluids, these plasticizers are often leached out resulting in a loss of flexibility. Although the use of polymeric plasticizers improves permanence, they are not as effective as lower molecular weight materials. The inability of the two polymers to mix thoroughly prevents close contact between the polymeric plasticizer and the elastomer, thus reducing optimum effectiveness.

The challenge in this type of application is to develop oil and fuel resistant elastomers that will also perform satisfactorily at low temperatures, down to at least −40°C. We have attempted to meet this challenge by grafting side chains onto the polymer chain to provide plasticization[13,14]. It was discovered that grafting of 2-ethylhexyl acrylate onto nitrile rubber led to significant improvement in low temperature flexibility as shown in figure 2. The grafting was accomplished during the normal cure cycle of the elastomer, thus eliminating the need of an additional costly synthetic step.

Figure 2 — comparison of low temperature flexibilities of original and oil aged samples for nitrile elastomers plasticized with monomeric plasticizer, with polymeric plasticizer, and with grafted plasticizer



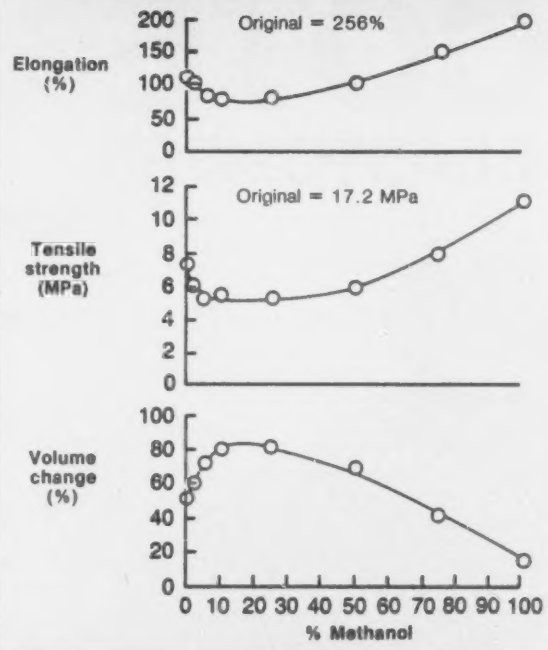
This method was shown to provide not only permanent plasticization, but also more than twice the effectiveness obtained by simple addition of a polymeric plasticizer. The improvement in flexibility was directly proportional to the amount of monomer employed. The structure of the monomer was also important in determining its effectiveness since variation in both the length and chemical composition of the ester side-chain led to changes in low temperature properties.

These results demonstrate that grafting is a feasible approach to developing elastomers which meet the challenge of having both oil resistance and low temperature flexibility. There may, however, be other approaches that can be used to reach the same goal.

Elastomers for fuel applications

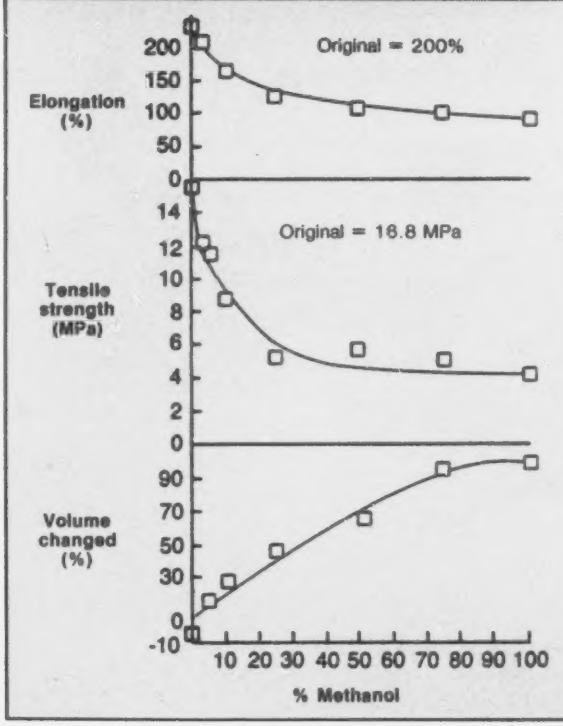
The challenge here is to develop elastomeric compositions that perform well in an increasing number of fuel blends. As was mentioned earlier, ethanol, methanol and methyl t-butyl ether, among other additives, are being blended into gasoline in order to improve the octane number or simply extend the gasoline. We have investigated the effects of these additives on the swell and tensile properties of elastomers[8,9,15]. It was found that in the case of fuel resistant elastomers exposed to alcohol-gasoline mixtures, the elastomer swell increases as the alcohol content of the gasoline is increased, reaching a maximum at alcohol concentrations between 10 to 40%, depending on the chemical structure of the elastomer. An example of our results is given in figure 3, showing the effects of increasing methanol concentration on volume change (swell), tensile strength and elongation of nitrile elastomer. Maximum swell of the elastomer occurs in a gasoline-methanol blend containing about 10% methanol. High swell of elastomers is undesirable not only because of dimensional instability but also because, as seen in the figure, it leads to a decrease in tensile strength and elongation. For most elastomers, the ultimate tensile and elongation values were found to be quantitatively related by simple linear equations to the volume fraction of the polymer in the swelled network. With the exception of fluorocarbon elastomer (in methanol-gasoline blends), the volume swell versus methanol concentration behavior, shown in figure 3, was observed for all fuel resistant elastomers exposed to both methanol-gasoline and ethanol-

Figure 3 — tensile elongation, tensile strength and volume change of nitrile elastomer after exposure to methanol/gasoline compositions



gasoline blends. The ethanol-gasoline blends are less severe than the methanol-gasoline blends in their effects on most fuel resistant elastomers. The results can be explained in terms of the solubility parameter concept. Fluorocarbon elastomers exhibited monotonic increase in swell with increase in methanol concentration as shown in figure 4. The maximum swell of about 100% occurred in pure methanol. The reason for the high swell was investigated using nuclear magnetic resonance (NMR) spectroscopy to determine the structure of methanol in pure form and in blends with polar and non-polar solvents. It was found that the hydrogen bonded structure of methanol is responsible for decreasing the overall solubility parameter of the alcohol to a valve equivalent to that of the fluorocarbon elastomers, thus causing the high swell.

Figure 4 — tensile elongation, tensile strength and volume change of fluorocarbon elastomer after exposure to methanol/gasoline compositions



The higher swell of the fuel resistant elastomers in alcohol-gasoline blends presents a challenge to develop new elastomers or new elastomer compositions that can withstand the more aggressive environment of the blends. Our response to this challenge was to develop a filler system that physically restricts swelling[18]. One promising approach is the use of platy fillers. These fillers form oriented plates in extruded elastomers. When elastomers containing platy fillers were exposed to swelling fluids, anisometric swelling was observed. A great deal of restriction in the swelling was seen in the plane of the oriented filler. If the filler is oriented in the critical dimension of the part, then the effective fluid resistance is improved. As seen in figure 5, the swelling restriction provided by talc in a nitrile elastomer formulation exposed to ASTM Fuel C is directly proportional to the volume fraction of the platy filler. This means that we can now control the dimensional stability of a fuel system elastomer part by simply adjusting the amount of platy filler without changing the chemical structure of the elastomer.

This approach provides solutions for certain elastomer parts exposed to fuel mixtures. Challenges and opportunities are still there for the development of other methods to make elastomer parts that will endure either gasoline-alcohol blends or pure alcohols. As most of you know, Brazil already uses 100% ethanol as automotive fuel. In the U.S., experimental fleets are currently running on methanol.

New or improved processing

The challenges in this area lie either in improving the current processing techniques to obtain better elastomer part performance or replacing current methods with faster, less expensive and/or less energy intensive

Figure 5 — effect of the volume fraction of platy filler on the swelling restriction of nitrile rubber

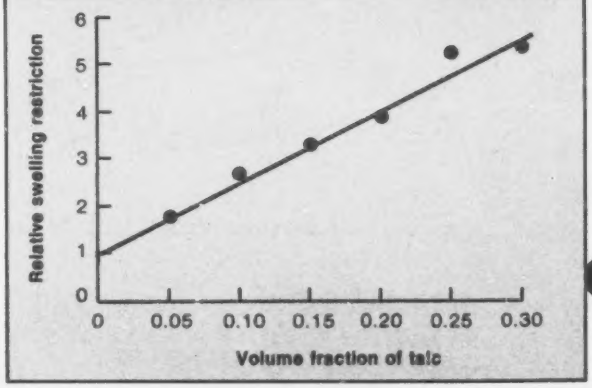


Table 2 — changes in properties of N330 carbon black after attrition

	Before attrition	After attrition
Particle size (A°)	260	150
pH	8.1	3.4
Critical surface energy of wetting γ_c (dyne/cm)	40.0	32.6

Table 3 — comparison of the properties at room temperature of carbon black reinforced polychloroprene obtained by the two mixing methods

Property	Cyclic mixing[a]	Conventional mixing[b]	Percent improvement (%)[c]
Tensile strength (MPa)	23.8	19.9	18.6
Ultimate elongation (%)	390	285	36.8
Fatigue life (cycle)	151,360	109,000	38.8
Permanent set (%)	0.90	3.25	72.3
Hysteresis at 100% elongation and room temperature	9.8	11.8	16.9
Freon-22 Permeability ($cm^4/s \cdot dyn$)	7.03×10^{13}	7.821×10^{13}	10.1

[a]Attrited N330 filled polychloroprene.
[b]N330 filled polychloroprene.
[c]Percent improvement (%) = [(a - b)/b] x 100%, where a = cyclic mixing and b = conventional mixing.

processes. The traditional processing of elastomers consists of three major operations: mixing, which is conducted normally in an internal mixer, followed by molding or extrusion into an article or part, and, finally, curing of the rubber article or part by chemical cross-linking of the matrix. Control of mixing of the ingredients is critical for obtaining uniform products with desired properties. Elastomers with the same composition can end up with different properties depending on the method and the degree of mixing. To improve the degree of mixing, we developed a mixing rule based on thermo-dynamic principles that takes into account not only the properties and amount of the ingredients in the formulation but also how they are mixed. Based on this rule, optimized conditions and procedures have been developed that lead to better distribution of the filler particles in the rubber matrix. The technique includes surface modification of the carbon black filler and a unique heating and cooling procedure for mixing the filler and rubber matrix[17,18]. The effect of attrition process on N330 carbon black is shown in table 2. In addition to smaller particle size, attrition (hot grinding) leads to a lower pH value for the slurry of the carbon black in water and a lower critical surface energy, γ_c. As a result, the interaction between this attrited filler and a polymer will be different. The ratio of surface energy of attrited N330 carbon black to that of neoprene is 1.03 as compared to 1.30 for the unattrited N330 black. This means that the attrited black is more compatible with neoprene.

The new mixing technique involves heating and cooling mixing cycles in a Banbury internal mixer or on a two-roll mill as shown in figure 6. The heating cycles are aimed at decreasing the microvoid concentration and enhancing polymer-filler adhesion, and the cooling cycles are aimed at improving the degree of mixing by shear stresses generated during mixing at lower temperatures. Better filler distribution and lower void concentration are observed in the case of the new mixing technology as compared to the conventional mixing. As a result, improvement in properties, such as tensile strength, ultimate elongation, fatigue life, permanent set and permeability, is obtained due to the improved mixing as shown in table 3. Perhaps the most significant is the improvement in the dynamic properties at low temperatures. Figure 7 shows the dynamic mechanical analysis (DMA) data of a neoprene (polychloroprene) composition mixed by two different methods. The glass transition for both samples is −37°C. However, the temperature sensitivities of the storage modulus of the two systems are quite different. The storage modulus of the conventionally mixed neoprene remains constant down to 40°C and then gradually increases as the tem-

Figure 6 — mixing temperatures on a two-roll mill using the cyclic mixing procedure

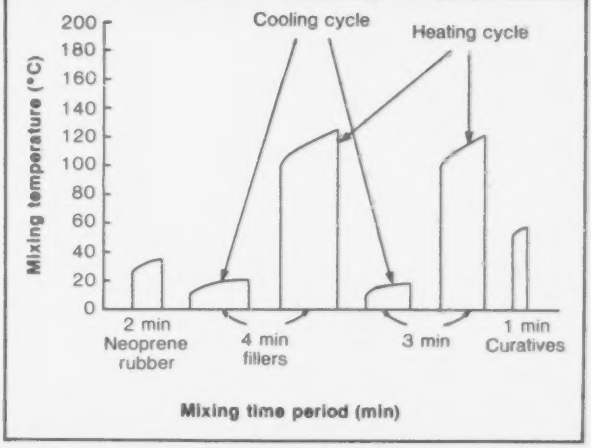
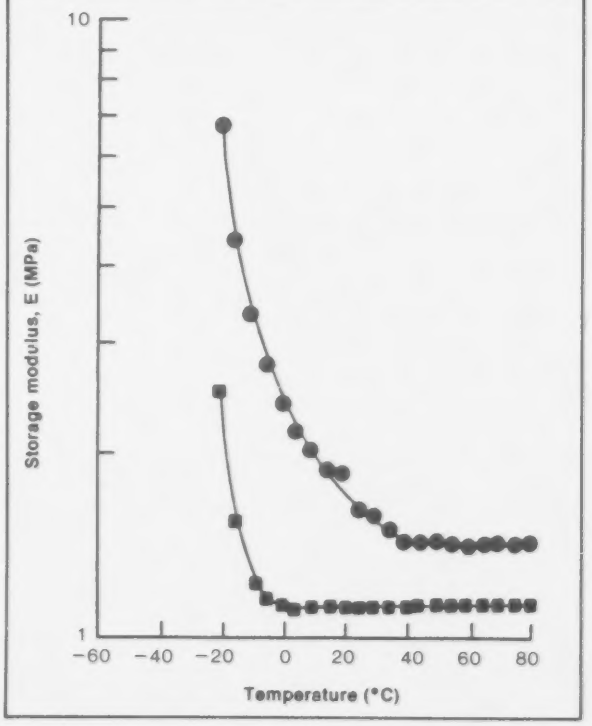


Figure 7 — storage modulus as a function of temperature for both the conventionally mixed (•) and the cyclically mixed (■) polychloroprene compositions



perature decreases and the polymer approaches the glassy state. In contrast, the storage modulus of the cyclically mixed neoprene remains constant down to −10° and then sharply increases to its glassy state value as the temperature decreases. In other words, through better mixing, the neoprene has better low temperature properties and less temperature sensitivity. Automotive suspension system components, such as the jounce bumper, could thus be designed using the improved mixed neoprene to provide the required energy absorption and spring rate and maintain these properties over a broader temperature range.

Improvements are also desired for the other two steps of elastomer processing, namely, molding and curing. The development of injection moldable elastomers and thermoplastic elastomers that have the required properties for automotive applications will lead to appreciable savings in time and energy and to less costly products. Also, microwave radiation can lead to savings in energy and even improved properties when used for the curing of specially designed formulations. Additional research is needed in all these areas to bring about the development of new and/or improved products and processes for use in the automotive industry.

Other challenges and opportunities

A few additional examples will be mentioned with regard to the potential needs of the automotive industry for specialty elastomers. These include conductive elastomers for new battery applications and for shielding of electronic circuits and dissipation of static charges. There is also a need for high strength oriented elastomer filaments and sheets for the purpose of energy storage and handling. However, the most pressing need is improved quality control during polymer synthesis to produce elastomers with consistent and uniform properties, i.e., the same molecular weight and molecular weight distribution, the same degree of branching, etc.

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Elastomer exhibitors

(continued from page 4)

Gates	806
Globe Automotive	265
Hercules	222
ICI Americas	1410
Imperial Clevite	1823
Indian Head Industries	2034
ITT Automotive	517
Kusan Mfg.	1179
Kuss Corp.	758
3M	617
Markel Corp.	2068
Master Industries	1868
Max Machinery	146
Mercer Corp.	602
Monsanto	1031
MTS Systems	241
Nordson	843/1404
Norton	1361
Ohio Rubber	157
Parker Seal	702
Plumley	1213
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RPM	2060
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W.S. Shamban	1544
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Sherwin-Williams	1709
Smithers Scientific	776
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Sumitomo Electric	1440
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Toyoda Gosei	723
Vernay Labs	1712
Wellman Inc	1428
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